MODELLING THE D.C. ELECTRICAL CONDUCTIVITY OF MORTAR

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ABSTRACT

The interfacial zone separating cement paste and aggregate in mortar and concrete is believed to influence many of the properties of these composites. This paper presents a theoretical framework for quantitatively understanding the influence of the interfacial zone on the overall electrical conductivity of mortar, based on realistic random aggregate geometries. These same ideas may also be used to approximately predict the fluid permeability of mortar.

INTRODUCTION

The D.C. electrical conductivity of mortar and concrete is an important measure of ionic diffusivity [1], via the Nernst-Einstein relation [2]. Diffusivity is of interest in connection with a range of issues related to durability, such as sulfate attack and chloride ion-induced corrosion of steel reinforcing bars [3]. Much recent work has been done on understanding how the microstructure of cement paste determines its electrical conductivity [4-9]. However, relatively little work has been done on how the conductivity of concrete depends on quantities like the number and arrangement of aggregate particles, and on the cement paste:aggregate interfacial zone [6,10-12].

In this paper, we are concerned with the (approximately 10 μm-1000 μm) length scale that adequately describes a typical mortar [13,14]. Within this framework, mortar (and concrete) can be viewed as a three-phase composite [15-17]: bulk cement paste, aggregate, and interfacial zone cement paste [see Figure 1], where all three phases can be thought of as uniform continuum materials. In such a three-phase composite model, the volume fraction assigned to the interfacial zone phase depends on what thickness is taken to define the boundary between the interfacial zone and the bulk cement paste. For values of the interfacial zone thickness around 20 μm, the interfacial zone cement paste occupies 20-30 % of the total cement paste volume, and therefore 10-15% of the total mortar volume [14]. Since the interfacial zone cement paste occupies a significant volume fraction, the different microstructure [18,19] and therefore different physical properties of this phase will certainly have an influence on the overall behavior of the mortar/concrete composite [20,21], especially since recent modelling and mercury injection experimental work have shown that the interfacial zone cement paste phase forms a continuous percolating channel [14,22].

RANDOM THREE-PHASE MODEL FOR MORTAR

More details of the following model are given in Ref. [23]. For the purposes of electrical conduction, the aggregate grains are simply inert obstacles to the flow of current. The basic

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model is then defined by two parameters: 1) the structure of the interfacial layer, and 2) the electrical contrast between this layer and the bulk cement paste. In this paper we replace the variable conductivity (because of varying porosity) interfacial zone region with a shell of fixed width and constant conductivity, σ_s, for the sake of simplicity. All the other cement paste outside the shell of thickness h is given the bulk cement paste value of conductivity, σ_p. Several authors have carried out experiments with planar or cylindrical aggregate shapes. A range of values for σ_s/σ_p have been found, from about 10 [11], assuming h = 20 μm, to 12-15 [12], assuming h = 100μm. This latter value for h seems much too large, since SEM investigations of the interfacial zone generally find that the porosity of the interfacial zone decreases to the bulk cement paste value by a distance of 30-50 μm from the aggregate grain surface [18,19].

Since there is no definitive value established experimentally for the value of σ_s / σ_p, we have chosen to allow this parameter to vary in the following computations, and studied the dependence of the composite conductivity, for a given sand content, on the value of σ_s / σ_p. However, based on the mercury intrusion and modelling results of Ref. [14], we have chosen h = 20 μm as the best value for the width of the interfacial zone. We emphasize that extracting the value of σ_s / σ_p from experiments will require an assumption for the value of h.

To obtain a model of a mortar with a realistic random sand grain arrangement, we used the system studied in Ref. [14] and shown in Fig. 1. From the experimently measured sand grain

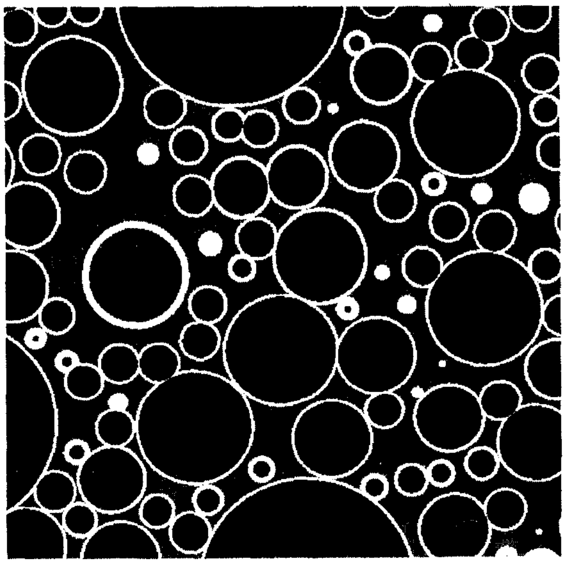

Figure 1: The structure of mortar, as represented by the random aggregate model. There are four sizes of sand grains (black), with diameters given in the text, and bulk cement paste matrix (gray). The thickness of the interfacial zone region (white) is 20 μm. The total volume fraction of sand is 54%.

size distribution used there, we chose four representative diameters: 250, 500, 750, and 1500 μm [23], with fractional volumes of 0.1895, 0.2233, 0.2317, and 0.3555 respectively of the total sand volume. For the maximum sand grain volume fraction studied, 54%, a total of 6500 particles were randomly placed and interfacial zones, of thickness 20 μm, were added to each grain.

Figure 2 shows the connectivity of the interfacial zone phase as a function of sand volume fraction. The y-axis, labelled "Fraction Connected", is just the fraction of the total interfacial zone volume, at a given sand volume fraction, that is part of a connected path across the sample. The interfacial zone phase first becomes partially connected at a sand volume fraction of about 36%, and essentially all of the interfacial zones are connected to each other by a sand volume fraction of 51%.

The conductivity of the random sand grain mortar model was computed using a random walk algorithm, used extensively in studies of disordered porous media [24] and composite materials [23,25-27].

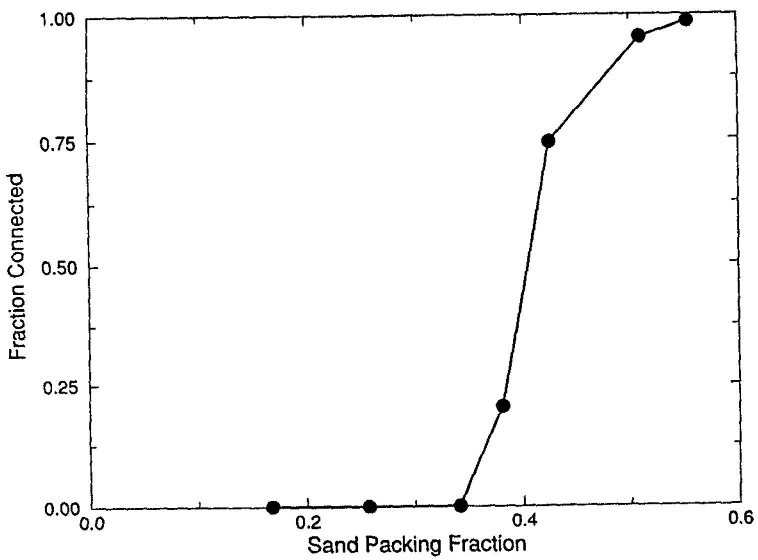

Figure 2: Percolation curve for random sand grain model, for a 20μm thick interfacial zone. The x-axis is the sand volume fraction, and the y-axis is the fraction of the interfacial zone phase that is contained in its percolating cluster.

ELECTRICAL CONDUCTIVITY RESULTS

Figure 3 shows the overall composite conductivity as a function of the ratio of the interfacial zone cement paste conductivity to the bulk cement paste conductivity, for a mortar with a sand volume fraction of 54%. The conductivity at $\sigma_s/\sigma_p = 1$ is that which would be obtained if the interfacial zone cement paste had the same porosity and therefore the same conductivity as the bulk cement paste. The presence of the insulating sand grains in this case reduces the overall normalized conductivity from 1 to 0.35. This is consistent with a 3/2 power law found in suspensions of spheres and many porous rocks, where the normalized conductivity goes like the 3/2 power of the conductive phase volume fraction. In this case, $(0.46)^{3/2} = 0.31$ [28,29].

The composite conductivity can be thought of as the result of a competition between the insulating sand grains, which tend to lower the overall conductivity, and the interfacial zone cement paste shells, which tend to raise the overall conductivity, when $\sigma_s > \sigma_p$. We note that in Fig. 3, the overall shape of the curve is concave down. The curve could at most be straight. This would be the case if the two phases, interfacial zone and bulk cement paste, were exactly in parallel. Since the microstructure is such that the two cement paste phases are not exactly in parallel, then the curve must be sub-linear, or concave down. As $\sigma_s/\sigma_p \rightarrow \infty$ the curve will asymptotically go to a straight line, as the interfacial zone phase will eventually dominate the conductivity.

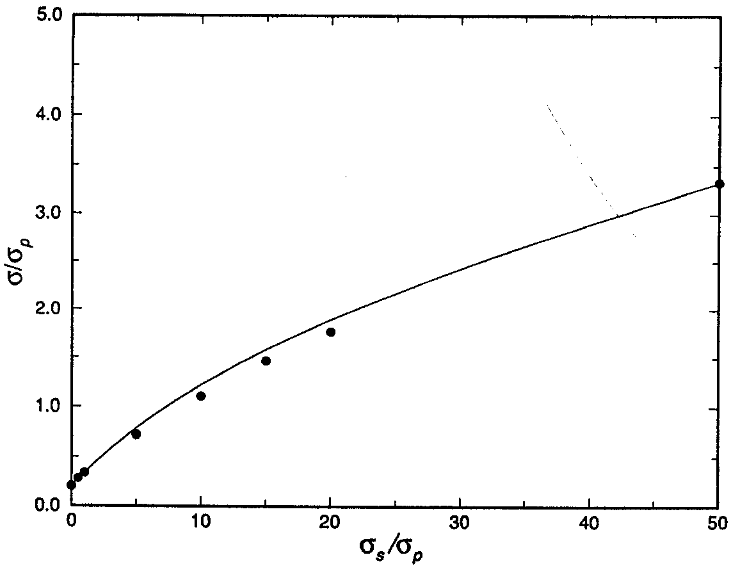

Figure 3: Composite conductivity for the random mortar model is plotted vs. the interfacial zone conductivity. [Both are normalized by bulk paste conductivity.] The solid dots are the numerical data, the solid line is the Padé approximant explained in Ref. [23].

To achieve an overall conductivity that is equal to the bulk cement paste conductivity, the value of σ_s/σ_p must be equal to approximately 8, as can be seen in Fig. 3. At $\sigma_s/\sigma_p = 20$, the overall conductivity is about 1.8. The solid line in Fig. 3 is a Padé approximant [23]. The fit to the data points is not perfect. However, the asymptotic slope of the Padé approximant for large values of σ_s/σ_p should be accurate, so that this curve can be safely extrapolated to predict the effect on σ/σ_p of much higher values of σ_s/σ_p. This becomes important below when we consider the effect of the interfacial zone on the fluid permeability of mortar.

A second important data set, more easily obtained by experimental techniques, will be obtained by measuring the conductivity of a mortar as a function of sand volume fraction, for a fixed value of σ_s/σ_p. One important aspect of such a data set is the dilute limit, where the sand volume fraction is low. The composite conductivity in this regime contains important information about the conductivity and size of the interfacial zone. This is the case because exact analytical calculations can be made of the influence on the overall conductivity of a few sand grains surrounded by an interfacial zone shell placed in a matrix [23]. The conductivity for a low volume fraction of sand (less than 10%) is an explicit function of h/b, where b is the sand grain radius, and of the parameter σ_s/σ_p [23]. For a given value of b and σ_s/σ_p, the conductivity takes the form

$$\frac{\sigma}{\sigma_p} = 1 + m\left(\frac{h}{b}, \frac{\sigma_s}{\sigma_p}\right) c\ , \quad c = \text{total sand volume fraction} \qquad (1)$$

When there is a distribution of sand sizes, m is replaced by $\langle m \rangle$, the average of m over the different values of b, for a given value of h and σ_s/σ_p.

From the results of Ref. [23], we find that at $\sigma_s/\sigma_p = 8.26$, for the sand size distribution used in this paper, $\langle m \rangle = 0$ [23]. At this value, adding a few sand grains would, to leading order in the sand volume fraction, have no effect on the overall conductivity, keeping its value at the bulk cement paste value. In Fig. 3, it was shown that a value of $\sigma_s/\sigma_p \approx 8$ was required to make the composite conductivity equal to the bulk cement paste conductivity at a sand volume fraction of 55%. This implies that there is information about the shape of the conductivity vs. sand volume fraction curve for this particular sand size distribution and interfacial zone width obtainable without further computation. For $\sigma_s/\sigma_p \leq 8.26$, such a curve must start out with negative slope, and σ/σ_p will always lie under the bulk cement paste conductivity. For $\sigma_s/\sigma_p >$ 8.26, the curve will start out with positive slope and always remain above the bulk cement paste conductivity. Using different sand size distributions will change this cutoff value but the overall picture should be similar, even for the large aggregate size distributions typical of concrete.

Figure 4 shows the results of computations of the overall mortar conductivity for different values of σ_s/σ_p (1,5,20) as a function of sand volume fraction. The predictions of the previous paragraph are shown to hold true, as 1 and 5 are smaller than 8.26, and 20 is larger than 8.26. The computed numerical values of $\langle m \rangle$ also agree within a few percent with the predicted values [23].

COMPARISON WITH EXPERIMENTAL EVIDENCE

Recently chloride diffusivity measurements have been made for cement pastes and mortars with several different sand volume fractions [30]. The ratio of the overall diffusivity to the cement paste diffusivity is, via the Nernst-Einstein relation, the same as the ratio σ/σ_p [2]. It was found that this ratio was on the order of 1-2, for both 0.4 and 0.5 w/c mortars, at about 50% sand content. Using Fig. 3, this result implies, assuming that the sand particle size distribution was similar to that used in our random mortar model, that σ_s/σ_p was roughly between

10 and 20, in agreement with the experimental results discussed earlier on flat aggregate interfaces [11-12].

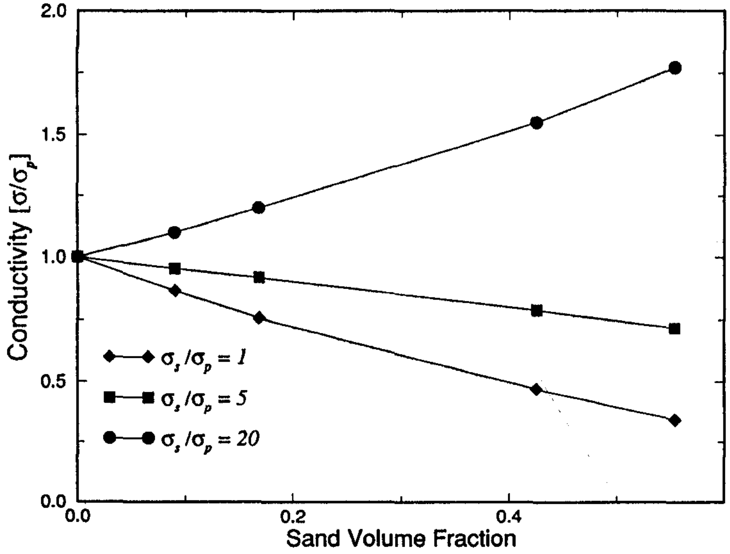

Figure 4: Composite conductivities (calculated by random walk simulations) for the random mortar model are shown as a function of sand concentration for several values of the interfacial zone conductivity. [Normalization is as in Fig. 3.]

Another paper that attempted to measure the conductivity of mortar as a function of sand volume fraction found completely different results [10]. We do not feel these results are trustworthy, as only a single frequency A.C. measurement was used, so that the true D.C. conductivity may not have been measured [5]. Also, the measured conductivities were significantly lower that the simple 3/2 power law [28,29] would predict, assuming that the interfacial zone conductivity was the same as that of the bulk cement paste matrix. In addition, the theoretical equation used in Ref. [10] does not give the correct dilute sand limit, as given in eq. (1) [23], so that even if the measurements were correct, any deductions made regarding the interfacial zone conductivity would be in error.

It is interesting to try to extend the modelling work to include fluid permeability. This can be done *approximately* via an electrical analogy between Ohm's law and Darcy's law [23,31]. The parameter K_s/K_p , the ratio of the permeability of the interfacial zone and the permeability of the bulk cement paste matrix, then takes the place of the conductivity parameter, σ_s/σ_p , and the equation to be solved is still Laplace's equation. One way to estimate the quantity K_s/K_p is to make use of the Katz-Thompson equation, which predicts the permeability of a porous medium in terms of its conductivity and a critical pore radius characteristic of the largest connected pores in the material, defined by a mercury intrusion experiment [1,32]. Neglecting constants of proportionality, the Katz-Thompson equation is

$$k \sim \frac{\sigma}{\sigma_o} d^2 \tag{2}$$

where σ/σ_o is the conductivity of the porous material relative to the conductivity σ_o of the conductive pore fluid it contains, and d is the critical pore diameter. If we assume that the value of d for interfacial zone cement paste is about 10 times as large as that for the bulk cement paste, in rough agreement with the available mercury intrusion evidence [14], and take the interfacial zone conductivity to be about 10 times larger than that of the bulk cement paste, in rough agreement with experiments on flat aggregates, then we would expect that the ratio K_s/K_p would be about 1000.

The largest value of K_s/K_p or σ_s/σ_p computed in Fig. 3 was only 50, but we can use the fitted Padé approximant, which should be more accurate in the large K_s/K_p limit, to estimate the overall permeability to be about 35 times that of the bulk cement paste. Data in Ref. [30] indicates that the permeabilities of mortars with about 50% sand are about 20-60 times higher than the cement paste matrix, again in reasonable agreement with the model prediction.

FUTURE WORK

An important goal of future work, based on the techniques and results of this paper, will be to develop a general equation for the conductivity/diffusivity of concrete. The inputs to such an equation would be: 1) the chemistry, water:cement ratio, and degree of hydration of the cement, in order to determine the bulk matrix conductivity, 2) interfacial zone characteristics, 3) aggregate size distribution and volume fraction, and 4) computations like those in this paper. With such an equation, the conductivity/diffusivity of a concrete could be determined with good accuracy at the mix design stage, based on fundamental physical parameters.

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